Articles

Hydrogenation of *trans*-Cinnamaldehyde with Hydrido-Carbonyl Osmium(II) Complexes of Chelating Phosphine Ligands

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A series of new hydridocarbonyl osmium(II) complexes, $OsHCl(CO)(PPh_3)(L\text{-}L)$[L-L=$Ph_2P(CH_2)_nPPh_2$ (n=1 (**1**), 2 (**2**), 3 (**3**), *cis*-$Ph_2PCH{=}CHPPh_2$ (**4**), and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ (**5**)] has been synthesized from $OsHCl(CO)(PPh_3)_3$ and chelating diphosphines. These complexes have been characterized by IR, ^1H NMR and elemental analysis. The catalytic activities of these complexes both for the transfer hydrogenation of *trans*-cinnamaldehyde with 2-propanol as the hydrogen donor, and for the selective hydrogenation of *trans*-cinnamaldehyde with H_2, have been examined. Complexes (**1**)-(**5**) were shown to have higher selectivities for the transfer hydrogenation of the C=O bond of aldehyde than for the transfer hydrogenation of the C=C bond of aldehyde. The selectivities for the transfer hydrogenation with 2-propanol as well as for the hydrogenation with H_2 have been found to decrease in the order **3>5>2>4>1**. Complex (**3**) has shown to possess almost 90% of the selectivity to cinnamyl alcohol for transfer hydrogenation. It is also found that there is a correlation between the ν(CO) of each complex and the hydrogenation, of the C=O bond of *trans*-cinnamaldehyde. Overall, the selectivities with the complexes (**1**)-(**5**) are greater for the transfer hydrogenation with 2-propanol than for the hydrogenation with H_2.

Although the homogeneous hydrogenation of C=O and C=C bonds of the organic compounds by ruthenium complexes has been widely investigated,[1] the analogous osmium complexes which are expected to have somewhat different catalytic properties have been relatively less studied. In general, because the 5*d* metals are known to form very stable bonds with molecules typically involved in the catalytic cycles, they have not been widely used as homogeneous catalysts. However, the osmium complexes can effectively be used as the catalytic precursors for the homogeneous hydrogenation, if the ligands of the complexes and the reaction conditions are properly selected. Examples of the homogeneous catalysis by the osmium complexes, however, have been mainly restricted to carbonyl clusters[2] and mononuclear hydrido-phosphine derivatives.[3]

We have previously reported the synthesis and catalytic activities of osmium complexes containing arsine ligands for the hydrogenation of propionaldehyde.[3b,3c] As a continuation of this research, we now report the synthesis and characterization of a series of new hydridocarbonyl osmium (II) mononuclear complexes, $OsHCl(CO)(PPh_3)(L\text{-}L)$[L-L=$Ph_2P(CH_2)_nPPh_2$ (n=1 (**1**), 2 (**2**), 3 (**3**), *cis*-$Ph_2PCH{=}CHPPh_2$) (**4**) and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ (**5**)], as well as their catalytic activities both for the transfer hydrogenation of *trans*-cinnamaldehyde with 2-propanol as the hydrogen donor and for the selective hydrogenation of *trans*-cinnamaldehyde with molecular H_2 under moderate reaction conditions.

Experimental

All manipulations were routinely carried out under nitrogen using conventional Schlenk techniques. Solvents were purified *via* fractional distillation under nitrogen or dehydration with Linde type molecular sieve 4 Å prior to use. $RuCl_3 \cdot H_2O$, PPh_3, $Ph_2PCH_2PPh_2$(dppm), $Ph_2PCH_2CH_2PPh_2$(dppe), $Ph_2PCH_2CH_2CH_2PPh_2$(dppp), *cis*-$Ph_2PCH{=}CHPPh_2$(dppv), and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$(dppf) were purchased from Aldrich Chemical Co. and used without further purification.

Physical measurements. The IR spectra (KBr disc) were recorded on a Analect FX-6160 FT-IR spectrometer. The ^1H NMR spectra were measured on a 300 MHz Varian Gemini 300 NMR spectrometer with $CDCl_3$, CD_2Cl_2, DMSO-d_6 as NMR solvents. Elemental analyses were performed by Micro-Tech Analytical Lab. at Skokie, Illinois, USA. The analyses of the products of catalytic reactions were carried out with a Hewlett Packard 5890 Series II gas chromatograph using HP-5 (crosslinked 5% PhMe silicone: 25 m × 0.2 mm × 0.11 μm film thickness) column and internal standard (n-decane) method. The chromatograph was connected to a HP 3394A integrator.

Preparation of $OsHCl(CO)(PPh_3)(Ph_2PCH_2PPh_2)$ (1). $OsHCl(CO)(PPh_3)_3$ (0.39 mmol, 0.405 g), which was prepared according to the known method,[4] and $Ph_2PCH_2PPh_2$ (dppm : 0.75 mmol 0.288 g) were refluxed in a flask containing 30 mL toluene under nitrogen for 3 hrs. The reaction mixture was then allowed to cool to room temperature, where yellow precipitates were formed. These precipitates were filtered, washed with *n*-pentane, ethanol, and again with *n*-pentane, and then dried *in vacuo*. Yield: 0.191 g, 42%.

Preparation of $OsHCl(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$

(2). $OsHCl(CO)(PPh_3)_3$ (0.39 mmol, 0.405 g) and $Ph_2PCH_2CH_2PPh_2$(dppe : 0.60 mmol 0.239 g) were refluxed in a flask containing 35 mL toluene under nitrogen for 5 hrs. The reaction mixture was allowed to cool to room temperature and was then filtered in air to remove any impurities. The filtrate solution was concentrated to *ca.* one half of the original volume, to which 30 mL of *n*-pentane was added to yield white precipitates. The precipitates were filtered, washed with *n*-hexane, ethanol, and again with *n*-hexane, and then dried *in vacuo*. Yield: 0.286 g, 80%.

Preparation of $OsHCl(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (3). $OsHCl(CO)(PPh_3)_3$ (0.39 mmol, 0.405 g) and $Ph_2PCH_2CH_2CH_2PPh_2$(dppp : 0.59 mmol 0.245 g) were refluxed in toluene (40 mL) under nitrogen for 3 hrs. The reaction mixture was filtered in air to remove any impurities and the filtrate solution was concentrated to *ca.* one half of the original volume. The addition of 30 mL of *n*-pentane yielded white precipitates which were filtered, and then washed with *n*-pentane, ethanol, and again with *n*-pentane. The final product was dried *in vacuo*. Yield: 0.229 g, 63%.

Preparation of $OsHCl(CO)(PPh_3)(Ph_2PCH=CHPPh_2)$ (4). $OsHCl(CO)(PPh_3)_3$ (0.39 mmol, 0.405 g) and $Ph_2PCH=CHPPh_2$ (dppv : 0.59 mmol 0.245 g) were refluxed in toluene (40 mL) under nitrogen for 3 hrs. The reaction mixture was filtered in air to remove any impurities and the filtrate solution was concentrated to *ca.* one half of the original volume. When 30 mL of *n*-pentane was added to the solution and white precipitates were obtained. The product was filtered in air, and then washed with *n*-pentane, ethanol, and again with *n*-pentane, and finally dried *in vacuo*. Yield: 0.229 g, 62%.

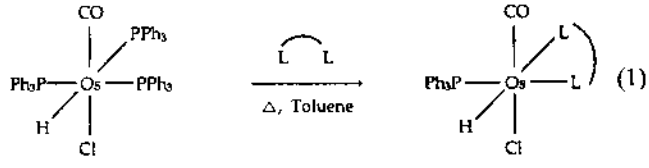
Preparation of $OsHCl(CO)(PPh_3)(Fe(\eta^5\text{-}C_5H_4PPh_2)_2)$ (5). $OsHCl(CO)(PPh_3)_3$ (0.39 mmol, 0.405 g) and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ (dppf : 0.60 mmol, 0.333 g) were refluxed in toluene (30 mL) under nitrogen for 2 hrs and then cooled to room temperature. The reaction mixture was filtered in air to remove any impurities and the filtrate solution was concentrated to *ca.* one half of the original volume. 30 mL of *n*-pentane was added to the solution and yellow precipitates were obtained. The product was filtered in air, and then washed with *n*-pentane, ethanol, and again with *n*-pentane, and finally dried in vacuo. Yield: 0.287 g, 69%.

Transfer hydrogenation of *trans*-cinnamaldehyde. A 30 mL toluene solution containing a catalyst (**1-5**) (0.02 mmol), *trans*-cinnamaldehyde (2 mmol), an internal standard (*n*-decane, *ca.* 0.28 g), and a hydrogen donor (2-propanol, 200 mmol, 11.8 g) was introduced into a Parr Series 4560 bench top mini reactor (Parr Instrument) with a gas inlet valve and a sampling valve. The system was purged three times with 40 psi nitrogen to remove air in the vessel. The temperature was raised to 110 °C. As soon as the reactor maintained constant temperature, stirring was started. This point was marked as time zero and sampling in an aluminum capped vial ($2cm^{-3}$) was performed periodically using a needle attached to the sampling valve and quenched at −20 °C to keep further reaction from proceeding, and quantitatively analyzed immediately by a gas chromatograph equipped with an FID detector.

Hydrogenation of *trans*-cinnamaldehyde with H_2 gas as a hydrogen donor. A 45 mL toluene solution containing a catalyst (0.02 mmol), *trans*-cinnamaldehyde (2 mmol), and an internal standard (*n*-decane, *ca.* 0.28 g) was introduced into a Parr Series 4560 bench top mini reactor with a gas inlet valve and a sampling valve. The system was purged twice with 40 psi nitrogen and then once with 40 psi hydrogen at room temperature to remove the air in the vessel. The temperature was raised to 90 °C. As soon as the reactor maintained a constant temperature, the hydrogen pressure was fitted to 74 psi (5 atm) and stirring was started. This point was marked as time zero and sampling into an aluminum capped vial ($2\ cm^3$) was performed periodically using a needle attached the sampling valve and quenched to −20 °C. The temperature was maintained constant throughout the reaction by a continuous supply of hydrogen gas from a high-pressure reservoir. The extracted samples were immediately analyzed by gas chromatograph equipped with an FID detector.

Results and Discussion

Synthesis and characterization of osmium(II) diphosphine complexes. $OsHCl(CO)(PPh_3)_3$, osmium(II) analogue of $RuHCl(CO)(PPh_3)_3$, reacts readily with an excess of the bidentate chelating ligands $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), *cis*-$Ph_2PCH=CHPPh_2$ (dppv) and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ (dppf) in boiling toluene to produce the corresponding new chelating diphosphine complexes, $OsHCl(CO)(PPh_3)(L\text{-}L)$ **1**: L-L= dppm; **2**: L-L=dppe; **3**: L-L=dppp; **4**: L-L=dppv; **5**: L-L= dppf, as shown in equation (1).



(1)

Elemental analysis and spectroscopic data of these complexes are represented in Tables 1 and 2, respectively. The possible ligand geometry around osmium(II) was unambiguously determined from ^1H NMR data and IR spectra along with the elemental analysis. For all the compounds, elemental analysis have shown a good agreement for each compound in Table 1. In the ^1H NMR spectra of all the complexes **1-5**, the metal hydride resonance signals were detected at high field chemical shift from −5.75 ppm (**4**) to −8.36 ppm (**1**). In all the complexes, the hydride resonance signals were observed as cleary resolved double quartets with coupling constant ($^2J_{H\text{-}trans\text{-}P}$) of *ca.* 84-99 Hz and coupling constant ($^2J_{H\text{-}cis\text{-}P}$) of *ca.* 12-21 Hz and 17-27 Hz. These results indicate that one of the chelating phosphorous

Table 1. Elemental analysis

Compound	C(%) Found (Calcd.)	H(%) Found (Calcd.)
1	58.71 (58.63)	4.30 (4.25)
2	58.97 (59.05)	4.43 (4.40)
3	59.56 (59.45)	4.49 (4.55)
4	59.70 (59.18)	3.90 (4.19)
5	59.40 (59.31)	4.29 (4.32)

Table 2. Spectroscopic data

Compound	^{1}H NMR (SiMe$_4$)			IR (cm^{-1})[a]	
	δ (Os-H) (ppm)	^2J(H,P)$_{trans}$ (Hz)	^2J(H,P)$_{cis}$ (Hz)	ν(C-O)	ν(M-H)
1[b]	-8.36	99.5	12.4 17.5	1934	1979
2[c]	-6.95	91.5	16.4 18.1	1913	1971
3[b]	-6.76	84.0	18.1 22.8	1903	2002
4[d]	-5.75	95.3	14.4 20.3	1927	1971
5[c]	-7.58	89.5	21.3 27.2	1909	2039

[a] KBr disc method. [b] In DMSO-d_6. [c] In $CDCl_3$. [d] In CD_2Cl_2.

atoms of the diphosphine ligand is *cis*-positioned to the hydride ligand and the other phosphorous atom is *trans*-positioned to the hydride ligand, which suggests that the osmium(II) complexes prepared in this work are *trans* isomers (Scheme 1). This relationship between coupling constant and ligand geometry of hydridophosphine metal complex was well established for decades.[5,6]

To our surprise, no structural isomers other than *trans* were detected by ^{1}H NMR for all of the compounds **1-5**. It is very noteworthy that analogous RuHCl(CO)(PPh_3)(L-L) complexes usually have two structural isomers, *cis*-isomer and *trans*-isomer, except for RuHCl(CO)(PPh_3)(dppv) and RuHCl(CO)(PPh_3)(dppf), which have shown to be *trans*-isomer only. For L-L=dppm, dppe and dppp, the complexes prepared in boiling toluene or stirring room at temperature in CH_2Cl_2 or 1 : 1 CH_2Cl_2-EtOH have shown to possess different isomer ratios.[5,7]

No remarkable changes of ν(CO) all the complexes after the preparations also mark the *trans*-isomer structure. Vibrational frequencies of the C≡O triple bonds were ranged from 1903 cm^{-1} (**3**) to 1934 cm^{-1} (**1**). If the trans position of a C≡O bond was occupied by good π-accepting ligand such as monodentate PPh_3 or chelating-PPh_2 moiety, Os(d orbital) → P(π* orbital) back donation should result in higher ν(CO) frequency. In addition to this, small ν(Os-H) bands were clearly separated from the strong ν(CO) bands for all the complexes to be within the range from 1971 cm^{-1} (**2** and **4**) to 2039 cm^{-1} (**5**). In the case of the analogous RuHCl(CO)(PPh_3)(L-L) complexes, all ν(Ru-H) bands were buried in strong ν(CO) bands.[5] Therefore, it is quite reasonable to assume the stereochemistry around Os(II) is the *trans* isomer same for all the compounds.

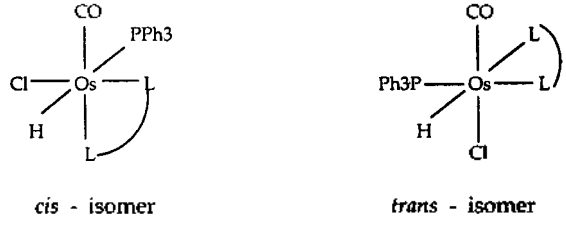
Hydrogenation of *trans*-cinnamaldehyde. Transfer hydrogenation uses organic compound as a hydrogen donor while normal hydrogenation by metal complex obtains its hydrogen from gaseous molecular hydrogen. Transfer hydrogenation of ketones in 2° Valcohol, usually 2-propanol (=*i*-PrOH), preceeded in the presence of KOH at the boiling point of solvent.[8] Spogliarich *et al.* performed transfer hydrogenation of cyclohexanone to cyclohexanol using cationic Wilkinson-type complexes, [Rh(diene)L_2]$^+$ (L=PMe_3, $PMePh_2$, PMe_2Ph, $PBzPh_2$, dppm, dppe, dppp, dppb, dppv, diop; diene=CON, NBD).

The activity of the complexes depended on the nature of the phosphine ligand used and showed the order dppe>dppp ≃ PPh_3>dppb ≃ diop ≃ dppv>PMe_2Ph>$PBzPh_2$>$PMePh_2$. They reported that higher catalytic activities had been obtained with bidentate ligands. The catalytic activity was also dependent on the number of methylene carbon atoms(n) in $Ph_2P(CH_2)_nPPh_2$, which was decreased with increasing *n*. Various ketones can be easily hydrogenated by hydrogen-transfer from 2-propanol in the presence of cationic [Ir(COD)(phen)]Cl (phen=1,10-phenanthroline).

Camus concluded that the positive charge on the metal probably assisted initial coordination of 2-propanol, the first step of the reduction.[10] Sumit Bhaduri *et al.* reported the transfer hydrogenation of α,β-unsaturated aldehydes, crotonaldehyde and *trans*-cinnamaldehyde, with 2-propanol as a hydrogen donor with ruthenium cluster, $Ru_4H_4(CO)_8L_4$ (L=P(n-Bu)$_3$, P(OEt)$_3$, PMe_3 or PPh_3).[11] They have found that the selectivities for the transfer hydrogenation of α,β-unsaturated aldehydes were greater at the C=O bond than the C=C bond.

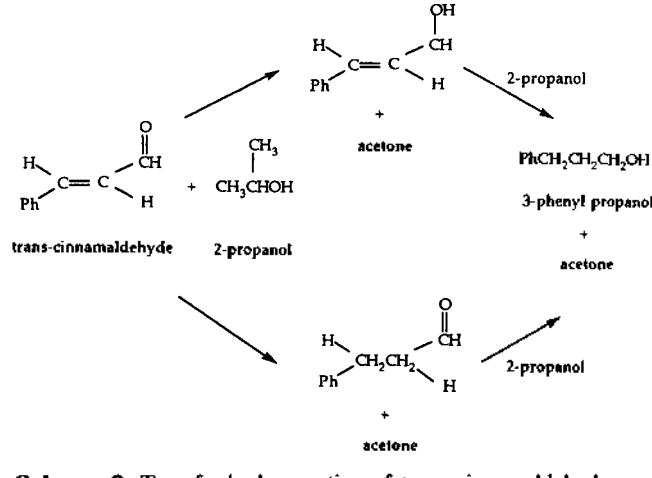
Trans-cinnamaldehyde serves two functional groups for hydrogenation. It means the hydrogenation reaction of the compound can be parallel as well as consecutive. The final product, 3-phenyl propanol, can be formed by two different pathways (Scheme 2). One pathway proceeds through the initial reduction of the C=O bond followed by the additional reduction of the C=C bond. The other pathway proceeds through the C=O bond reduction after the C=C bond reduction.

In this experiment we monitored the amount of cinnamyl alcohol and hydrocinnamaldehyde as well as that of 3-phenyl propanol to study the selectivities of both the hydrogenation with molecular hydrogen gas and the transfer hydrogenation with 2-propanol as a hydrogen donor with newly prepared neutral diphosphine Os(II) complexes. The results for both reductions are summarized in Tables 3 and 4. Time courses for complexes, 3, 4 and 5, are also



cis - isomer *trans* - isomer

Scheme 1.



Scheme 2. Transfer hydrogenation of *trans*-cinnamaldehyde.

Table 3. Selectivities of osmium complexes for cinnamyl alcohol formation in the hydrogenation and transfer hydrogenation

Compound	Selectivities for cinnamyl alcohol[a]	
	Hydrogenation	Transfer Hydrogenation
1	61	63
2	69	77
3	84	91
4	65	74
5	72	80

[a] [amount of cinnamyl alcohol/amount of (cinnamyl alcohol+hydrocinnamaldehyde)] × 100%. Above values are taken just before the formation of 3-phenylalcohol.

Table 4. Conversion (%) in the hydrogenation and transfer hydrogenation

Compound	Conversion(%)	
	Hydrogenation[a]	Transfer Hydrogenation[b]
1	25	10
2	30	19
3	71	39
4	28	20
5	100	92

[a] [amount of product/initial amount of substrate] × O 100% after 2hrs. [b] [amount of product/initial amount of substrate] × O 100% after 3hrs.

represented in Figures 1 through 6. In general, the C=O bond was more easily reduced than the C=C bond in both of the hydrogenation reactions. Such observation might not be unusual, since the C=O bond is sterically less hindered than the C=C bond in this case and the C=O bond can easily coordinate to the Os(II) center. It is believed that the rate determining step in the transfer hydrogenation is the hydrogen-transfer step from the hydrogen donor molecule.[12] From Tables 3 and 4, it is noted that the selectivity for the reduction of the C=O bond is greater for the transfer hydrogenation than the hydrogenation with gaseous H_2. Because the sterically more hindered 2-propanol is coordinated to the metal center during the transition state of the transfer hydrogenation, while the sterically less hindered molecular

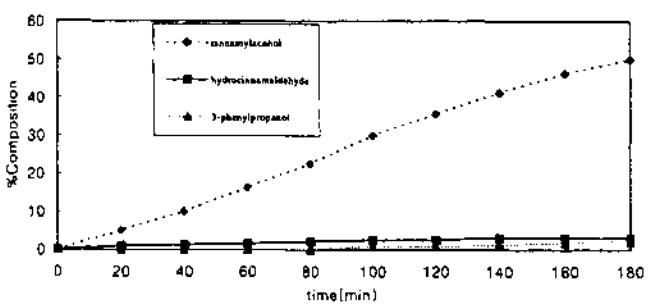


Figure 1. Transfer hydrogenation of *trans*-cinnamaldehyde with complex (3).

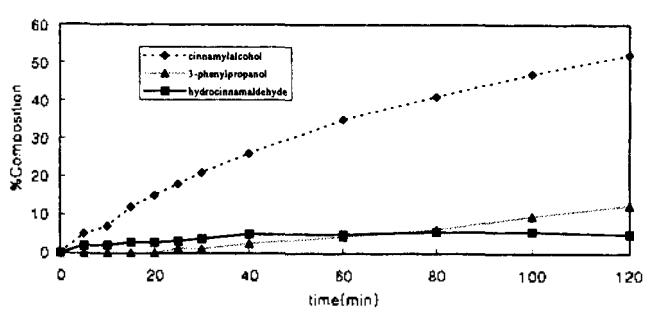


Figure 2. Hydrogenation of *trans*-cinnamaldehyde with complex (3).

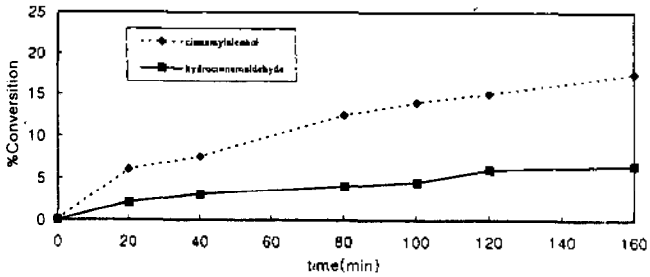


Figure 3. Transfer hydrogenation of *trans*-cinnamaldehyde with complex (4).

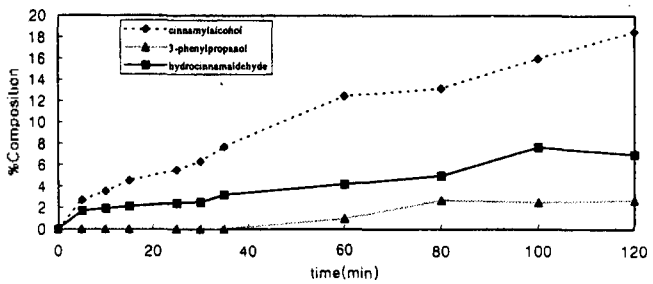


Figure 4. Hydrogenation of *trans*-cinnamaldehyde with complex (4).

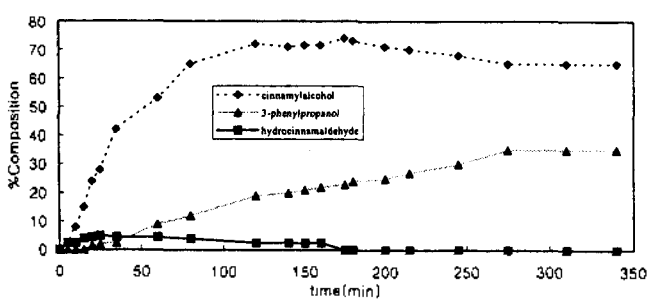


Figure 5. Transfer hydrogenation of *trans*-cinnamaldehyde with complex (5).

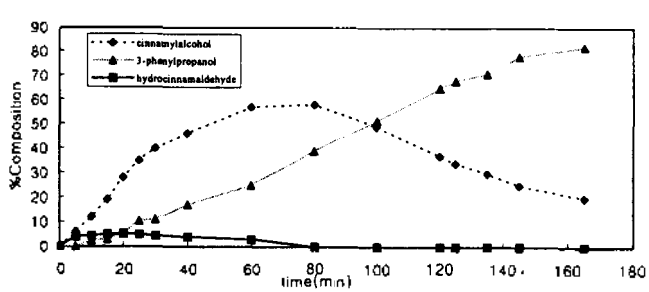


Figure 6. Hydrogenation of *trans*-cinnamaldehyde with complex (5).

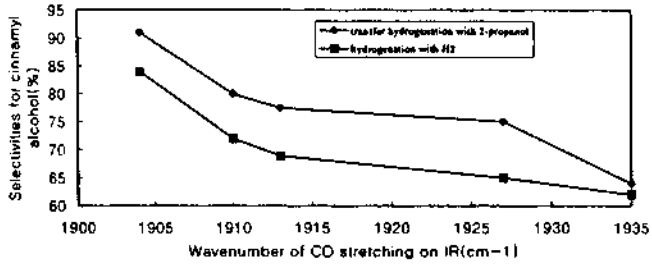


Figure 7. Plots of selectivities for cinnamyl alcohol *vs.* ν (CO). ◆ (transfer hydrogenation with 2-propanol), ■ (hydrogenation with H_2)

H_2 coordinates at the metal center for the hydrogenation with H_2, the energy difference between these transition states might lead to a higher cinnamyl alcohol to hydrocinnamaldehyde ratio for the transfer hydrogenation than that of the hydrogenation with gaseous H_2.

Overall, complexes **1-5** have shown the same selectivity trend for both the transfer hydrogenation of *trans*-cinnamaldehyde with 2-propanol and the hydrogenation of *trans*-cinnamaldehyde with H_2 gas. The selectivities for C=O bond were found to decrease in the order **3>5>2>4>1** as shown is Table 3. Complex **3** has shown to possess almost 90% of selectivity. It is noteworthy to implicate some relation between the vibrational frequency ν(CO) in IR spectra for complex and the selectivity for cinnamyl alcohol as shown in Figure 7. It is very difficult to quantify these observation. However, we may explain this phenomena as follows. The vibrational frequency ν(CO) for metal carbonyl complex represents the degree of metal to C≡O back donation.[13] High ν(CO) indicate weak metal-carbon bond, indicating a strong C≡O bond. A lack of the strong metal to ligand back donation implies the lower electron density of the metal center and the relative lower ability to bind locally negatively charged 2-propanol or organic C=O bond of the substrate localy, which thus makes cinamyl alcohol formation less easy.

In summary, the Os(II) complexes of the diphosphine ligands catalyze the transfer hydrogenation and the hydrogenation with H_2 gas of *trans*-cinnamaldehyde. The selectivity of the catalytic reaction depends on the complex, especially the coordinated diphosphine ligand. Such diphosphine ligand plays a key role in catalytic cycle in terms of the electronic and steric effects.

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